START

1100 AREA SOIL-GAS ANALYSIS PROTOCOL

BACKGROUND

EPA's experience with CERCLA/SARA investigations has shown that subsurface and ground-water contamination by volatile organic constituents, particularly chlorinated hydrocarbons represents one of the most persistent contamination issues under consideration throughout the US. Volatile organic contamination of the ground water has already been identified at several locations on the Hanford Site and is suspected at others. These contaminants are typically identified through ground-water monitoring and surveillance programs; however, direct measurement of ground-water contamination through drilling of sampling wells is a very expensive and time consuming operation. High drilling costs have been a particularly serious problem on the Hanford Site. Well sampling techniques, while unquestionably necessary to provide hydrologic data and evidence of regulatory compliance, may nevertheless be limited in effectiveness for rapidly diagnosing the extent of plume spread of volatile organic contaminants particularly in areas where the ground water is relatively deep with correspondingly high costs per well. The soil-gas method was developed as a cost effective alternative for generating relatively dense data grids on a short time scale. The soil-gas method can be used effectively as a preliminary screening tool for aiding in the optimal placement of monitoring wells. The soil-gas method has been adapted by PNL to the needs of the Hanford Site. Areas of specific applicability at Hanford include but are not limited to potential solvent contamination of the ground water in the 1100 Area and Horn Rapids Disposal, extensive carbon tetrachloride contamination in the 200W Area, chlorinated hydrocarbon contamination at the Solid Waste Landfill, solvent contamination in the 300 Area, trichloroethene contamination from the White Bluffs Acid Pickling Crib, and possible solvent contamination in other parts of the 100 Area.

In favorable cases the soil-gas method has been found to correlate well with directly measured concentrations in ground water. This is particularly true for chlorinated species with favorable Henry's Law properties. Under ideal conditions the soil-gas concentration of each species present in the ground water will decrease linearly from the Henry's Law value at the water table to zero at the soil-air interface. The method has been far less successful with non-chlorinated species which tend to be consumed by biological activity. Some of the other factors which influence soil-gas profiles include: geologic properties of the vadose zone, soil moisture content, temperature, depth to ground water and ground-water flow rate, phase separation, soil organic content, temperature and temperature gradients, water table oscillations, lithology of the aquifer, barometric effects, and rainfall. Interpretation of soil-gas data may thus be complex and highly site specific. Site-specific experience in representative geological regimes and if possible careful comparisons with available "ground truth" (i.e. grab samples from wells) is thus crucial to full utilization of the method. This may be accomplished on the Hanford Site by careful studies at the Solid Waste Landfill which has favorable properties as a "ground truth" source with well

documented and reasonably constant contamination by at least five chlorinated hydrocarbon species at readily detectable levels. The Solid Waste Landfill is also well documented with respect to geologic and hydrological characteristics and represents a reasonably typical Hanford setting. A detailed soil gas survey of the Solid Waste Landfill and will be completed and evaluated before start of soil gas work in the 1100 Area.

SUMMARY OF METHOD

At present no universally or regulatorily accepted method is available for the performance of soil-gas surveys, consequently considerable latitude is possible for the exact choice of methodology employed. Soil-gas probes are typically emplaced 3 to 6 feet below the surface. If possible all samples should be taken at the same penetration depth to facilitate interpretation. In the PNL procedure to be employed at the 1100 Area sites, a constant depth of 4 feet will if possible be employed for all samples. Probe penetration of less than 36" will be considered to be penetration refusal and the probe will be moved to a new location. Gas samples drawn through the probe by a low-volume pump may be collected either by a gas sampling syringe or a sorption trapping device (i.e. Tenax, charcoal, or both). The sorption trap method offers much greater sensitivity at the expense of analytical complexity. The syringe method is of adequate sensitivity and is in general preferable because of its simplicity, speed, and reliability. All work performed by PNL will use the direct sampling method employing gas-tight syringes of volumes ranging from 0.1 to 5 ml. Samples will also be collected in 300-1000 ml flow-through gas sampling flasks so that repeat measurements may be made in the laboratory for improved dynamic range. Analysis of the drawn sample is performed by gas chromatography (GC) employing detectors with both broad spectrum sensitivity (i.e. flame ionization [FID]) and halogen selectivity (i.e. electron capture [ECD]). The electron capture detector in particular is an extremely sensitive device making it possible to use relatively small sample volumes. The GC system employed by PNL uses a split inlet with separate capillary columns connected to ECD and FID detectors. The analytical work itself is performed according to appropriate EPA guidelines for the analysis of volatile organics by gas chromatography. Suitable calibration standards are available to permit identification and quantification of the most commonly detected species. These include at a minimum the following compounds: 1,1,1 trichloroethane (TCA), carbon tetrachloride (CCl4), trichloroethylene (TCE), 1,2 dichloroethane, 1,1 dichloroethane, tetrachloroethylene (PCE), cis and trans dichloroethylene, chloroform, methylene chloride, chlorobenzene, benzene, toluene, ethyl benzene, m+p-xylene, o-xylene, methylethyl ketone (MEK), methylisobutyl ketone (MIBK), hexane, heptane, and octane. Calibration for other species may also be performed if necessary to identify unknowns detected during actual field work.

SAMPLING

Design of Sampling Grid

Site specific soil-gas survey plans have been presented in the 1100-EM-1 Operable Unit Sampling and Analysis Plan. This plan will be utilized as general guidance. Sampling results, however, will be used for real-time guidance for modification of the basic sampling plan. That is, grid size may be increased or reduced during the course of the survey to better define the locations of maximum concentration. A survey will be conducted by Kaiser Engineering prior to commencement of field work. Stakes emplaced by the surveyors will be used as reference points. Soil-gas probes will be emplaced as close as possible to the stakes. Deviations from those locations resulting from either refusal problems or authorized changes in the grid size will be duly noted in the field records with distance and direction from the nearest survey stake recorded.

Sample Probes

Sample probes are constructed according to the design of LaBrecque et al. Detailed machine drawings of the probe and associated hardware have been provided by Kerfoot and Barrows. The PNL version of the design has been modified somewhat to provide a sacrificial penetrator tip slipped over the end of the probe to prevent clogging of the sampling ports during probe entry. Other design improvements include a larger diameter probe body (1") to provide better durability in rocky soil, the use of Acme threads in place of pipe threads, and Swagelok type fittings on the interior plumbing to eliminate leak problems associated with vibration. The probes and tips are mass produced in the 300 Area Machine Shop. Several different probe sizes ranging from 5 to 8 feet have been used. For the 1100 Area work 6 foot probes will be used exclusively. The probes are of all steel construction to minimize carryover of volatile organics. Following assembly, the probes are pressure leak checked. Probes will be cleaned with methylene chloride followed by acetone and methanol to remove machine oil prior to final assembly. Probes will be placed in the ground to a nominal depth of 4 feet by hammering with a vibratory hammer. Both electric and pneumatically powered percussion hammers are available. A slide hammer is also available for manual probe insertion in remote areas. Following penetration to the required depth, the probe will be withdrawn 2" to allow separation from the sacrificial tip. For work in excessively rocky soil a powered auger with a 6" bit can be used facilitate entry of the probe. In that case, the auger will drill a hole to within 12" of the required depth. The probe will then be emplaced in the hole and hammered to the required depth. The hole will be carefully backfilled with spoil and firmly tamped down. A sharpened solid steel bar may also be used in rocky conditions to create a channel for probe entry. In that case the probe is simply reinserted in the same hole and hammered to the required depth. That procedure greatly reduces stress on the probes and increases their working lifespan. In Either case the probes should be left in the ground for at least 12 hours prior to sampling to allow recovery of the soil gas profile following penetration. The probe will be removed

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by reverse hammering or with a mechanical jack if necessary after completion of sampling.

It should be noted that the above discussion assumes that the work will not be performed in a radiological hazard zone. The 1100 Area work is not expected to involve any unusual radiological hazard. Special precautions with respect to personnel safety and equipment decontamination will be needed for work in contaminated areas.

Sample Collection

The sample collection train consists of a 1/8" diameter stainless steel tube connected to a gas sampling bulb with Cajon type o-ring sealed high-vacuum fittings. Gas is drawn through a 300-1000 ml gas sampling bulb by a battery powered pump. The pump used is an Aircheck Model 224 PC-3 (1-4 LPM). The Aircheck pump will be used at a flow rate of 1 LPM. The rotameter flow meter on the pump may be used to verify the presence of flow through the probe. A very sensitive pressure sensor in the pump shuts the pump down automatically if the pump starts to pull vacuum. The sample train should be tested by plugging prior to each use to verify that it is leak tight. It will then be connected to the probe and flow verified. In the event that the probe tip is found to be plugged with soil, remedial measures will be implemented. These can simply include lifting the probe a few inches and tapping to clear the tip. If that procedure is not successful, a short burst of compressed may be used to remove the obstruction. If flow is still obstructed, the probe will be removed, cleared and reinserted in, or as close as possible to, the same hole. To collect a sample, the pump will be run for a period of time sufficient to completely purge the dead volume of the system which is typically dominated by the sample bulb volume. A nominal purge time of at least 7 minutes prior to sampling should be allowed to completely purge the gas sampling bulb. No internal combustion engines should be operated in the immediate vicinity during sample collection. A photoionization detector (HNU) will be connected to the output of the sampling pump during the purge period. The HNU reading will be recorded in on the field records at the end of the purge period. A high HNU reading will serve as a warning to the analyst to use a smaller sample to avoid overloading the gas chromatograph. The sample bulb will then be valved off, labeled, and removed to the motor home for analysis. Sample location, pump time, and any other pertinent observations including meteorological conditions will be recorded on the field record sheets and field notebook. The probe may be cleaned and moved to a new location while the sample is being analyzed. Prior to reuse the probe tip is unscrewed from the body of the probe, cleaned, and inspected to verify that the fittings are tight. The air sampling pump should be placed on its battery charger at the completion of each day's sampling.

ANALYSIS

Mobile Laboratory

Analysis of the samples will be performed as soon as possible following receipt of sample. Samples should not be held more than 24 hours without analysis. All analytical equipment will be located in the PNL Environmental Sciences Department Mobile Gas Chromatography Laboratory. This facility is centered around an Explorer 30 motor home. If possible it is preferable to locate the motor home within 50 feet of usable external power so that the 220V umbilical system may be used thus avoiding the need to arrange in-field fuel refills and generator maintenance. Alternatively, a 15 KVA trailer mounted generator is available to the project and has been used successfully to support field use of the motor home. The motor home should also, if consistent with electrical requirements, be located in a reasonably central location near the site under investigation so that only one setup period is needed. All of the 1100 Area sampling locations are within a 5 minute driving time of the PNL Sigma 5 facility which is the normal home base for the motor home. All analytical work will thus be performed at that central location.

Instrumentation

Samples will be analyzed with a Hewlett-Packard Model 5880A gas chromatograph. The GC is equipped with two identical J&W DB-624 30 m X 0.53 mm fused silica capillary columns. The DB-624 columns are coated with a cross-linked and bonded stationary phase composed of cyanopropyl, phenyl, dimethylsiloxane. The two columns are teed together at the inlet and are routed to separate electron capture (ECD) and flame ionization (FID) detectors. Sample introduction is via a Tekmar Model LSC-3 purge and trap unit. Samples can be introduced into the LSC-3 in either gaseous or liquid form through the same inlet fitting thus permitting calibration of the system by VOA water standards. The LSC-3 contains a Tenax sorption trap. Samples are thermally desorbed from the Tenax trap and transferred to the columns through a heated transfer line. The LSC-3 has been modified by addition of a pneumatic valve actuator to permit full automation of the purge and trap cycle by the GC run table. The HP 5880A is equipped with two separate integrators to simultaneous integrate data from both detectors.

Analytical Methodology

At the present time there are no standard reference analytical methods for analysis of soil gas samples. Analytical measurements will be performed in accordance with the general guidelines set forth in EPA Method 502.2. There are several significant exceptions to the method as presented. Method 502.2, as written, is a capillary column gas chromatography method for analysis of volatile organic compounds in water. The method employs a Hall electrolytic conductivity detector (HECD) for halogen selectivity) in series with a photoionization detector (PID) for detection of a broad range of compounds. The detector

used in this work for halogen selectivity is an electron capture detector (ECD). The ECD is considerably more sensitive than the HECD for the most common chlorinated solvent contaminants and has adequate halogen selectivity to satisfy the goals of the method. The flame ionization detector on the other hand is less selective than the PID providing maximum assurance of broad spectrum response. Incompatibilities in makeup gas require that the two detectors be run in parallel rather than in series which is clearly a disadvantage of the configuration. The method of sample introduction has been modified to accommodate either gas or water samples. The purge and trap cell is filled with 5 ml of boiled deionized water. Gas samples in gas-tight syringes are introduced through the normal sample inlet of the purge and trap unit, bubbled through the water, and passed through to the sorption trap. The initial injection is followed second volume of ambient air to clear the syringe and sample inlet of any residual analyte. The GC is then cycle through a complete purge and trap cycle according to EPA guidelines and manufacturers recommendations. Calibration is performed as described below with water samples; however, the units used for calibration are micrograms of total sample recovered rather than concentration. Gas concentrations can then be manually calculated by dividing by the injected volume.

The quality of soil gas data will be assessed through the use of replicate measurements, blanks, standards, and interlaboratory splits as specified in the Quality Assurance Plan of the 1100-EM-1 Operable Unit Remedial Investigation Feasibility Study Work Plan. In general, at least one replicate measurement and standard shall be analyzed for every twenty points, blanks shall be run for every tenth sample and an interlaboratory split shall be collected for every twentieth sample.

Calibration

External calibrations will be performed with water samples prepared according to standard methods and introduced into the purge and trap unit according to manufacturers recommendations. Linearity will be verified for five concentration ranges. Working standards will be prepared by dilution with boiled, deionized water of stock solution of the analytes of interest in dissolved in methanol. High end calibrations will be performed for the following species at the specified concentrations: chloroform (10 ppb), 1,1,1 trichloroethane (6 ppb), tetrachloroethene (3 ppb), carbon tetrachloride (3 ppb), and trichloroethene (6 ppb). Two, five, ten, and twenty-fold dilutions with boiled, deionized water will then be made to verify linearity. Response factors will be computed for both the ECD and FID channels. Detection limits will be calculated by reference to the low-end standard and ambient air blank. Calibration factors will be verified once daily prior to sample analysis with a mid-range standard. In addition to the species discussed above, stock solutions will also be available for the following analytes: 1,2 dichloroethane, 1,1 dichloroethane, cis and trans dichloroethylene, methylene chloride, chlorobenzene, benzene, toluene, ethyl benzene, m+p-xylene, o-xylene, methylethyl ketone, methylisobutyl ketone, hexane, heptane, and octane. Dilutions of those analytes shall be used for accurate determination of retention time; however, those species will not normally be quantified

unless found in actual soil gas samples.

Validation

The validity of the calibration procedure will be validated by two independent methods:

1.) Gas standards for the analytes of interest will be prepared by addition of 10 microliter samples of stock solution in methanol to a gas sampling bulb of accurately known volume. The volume of the bulb will be determined by filling with water and weighing. Evaporation of the methanol sample solution inside the bulb will produce a dilute analyte-air mixture of accurately known concentration. Bulbs will be heated to 100 C for at least 1 hour to promote complete mixing. Samples drawn from the gas sampling bulb will be injected into the GC and compared with samples of the same analyte introduced into the purge and trap unit as water solution.

2.) An alternate method used for validation will employ a VIC-Metronics Model 340 Dynacalibrator to produce a gas stream of accurately known concentration. Gas permeation tubes containing MIBK, PCE, CCl4, TCA, TCE, and MEK are available for the for the Dynacalibrator. Dilution flows will be accurately measured with an SKC-West Accuflow Digital Film Calibrator. The Dynacalibrator effluent flow stream will be routed through a gas sampling bulb. After complete temperature equilibration of the Dynacalibrator and purging of the gas sampling bulb, the bulb will be valved off and used as a calibrated sample source for comparison with the calibrations obtained with water solutions. Separate calibration runs will be made for each permeation tube.

Blanks

Two types of blanks must be considered, i.e., water blanks and gas blanks. At least one set of each type of blank will be run prior to initiation of sample analysis on a daily basis. More frequent analysis of blanks will be performed if blank contamination is detected or suspected. Water blank analysis will be performed on samples of reboiled deionized water produced in the Sigma 5 Building. Gas blanks will consist of ambient air drawn through the entire sampling train set up at least 0.5 m above the ground surface, collected, and treated as a sample. Care must be taken in collecting ambient air samples to insure that the air sampled is pristine.

Sample Analysis

Samples will be analyzed as soon as possible following receipt in the motor home (i.e. within 30 minutes). In the event that some delay in analysis is unavoidable, the sample will

be stored in the refrigerator until use. Samples should be allowed to return to room temperature before analysis. Samples will be withdrawn from the gas sampling bulb with a gas-tight syringe fitted with a 2" sampling needle. In areas with suspected high contamination, an initial sample of 200 microliters will be taken with a 1 ml syringe to avoid accidental overload of the GC. Based on the result, a scaleup to 5 ml may be performed. At least 10% of the samples showing positive detection on the 5 ml or smaller sample should be run in duplicate to provide data for estimation of precision. Syringes and gas sampling bulbs will be vacuum flushed prior to reuse. Bulbs should be disassembled and baked prior to reuse if they have been exposed to contaminant levels in excess of 5 ng/ml.

DATA QUALITY OBJECTIVES

The soil gas survey method is a cost effective screening tool intended as a supplement to (not a replacement for) well sampling. The goal of the program is thus to obtain data of adequate quality to determine if certain types of contaminants exist in the subsurface and provide a reasonable estimate of the areal extent of the contamination. The procedure should if possible have adequate sensitivity to detect contaminants in the ground water at or below their respective MCL's; however, that goal is only possible for a limited number of species including carbon tetrachloride, chloroform, 1,1,1 trichloroethane, tetrachloroethene, and trichloroethene. The spacing of the data grid should be sufficiently fine to permit detailed contour plotting needed for the siting of wells. A spacial resolution of 1/2 the distance to the ground water is useful as a guideline for minimum spacing of sampling points. Limitations of the method should be recognized. The soil-gas survey method is not sensitive to species of limited volatility or any inorganic or radioactive species. The method has been found to be best applied to halogenated (primarily chlorinated) species because of bacterial or other degradation effects for most nonhalogenated species. The method cannot easily distinguish between ground-water and vadose zone contamination. Analytical sensitivity is limited by distance to ground water. Analytical sensitivity is otherwise limited on a species by species basis by a variety of physical parameters for the individual analytes such as Henry's Law constant and diffusion coefficient. While correlations with ground-water concentration can be made, the method should normally be used only as a relative screening tool. Attempts to derive quantitative estimates of ground-water concentrations should be approached with extreme caution. Accuracy and precision of data should be consistent with best available measurement technology and EPA guidelines for the measurement of VOA's in water. Precision of individual measurements should be between 5% or better depending upon the level detected.

QUALITY ASSURANCE

Work will be performed according to the quality assurance provisions of PNL-MA-70. Additional quality assurance guidelines shall be as specified in the Quality Assurance Plan

of the 1100-EM-1 Operable Unit Remedial Investigation Feasibility Study Work Plan.

DATA REPORTING

Soil gas concentrations will be reported in micrograms of analyte per liter of air. Air volume will be that measured with a gas sampling syringe at ambient temperature and pressure. Data will be plotted on a copy of the site map and suitable contours drawn by hand. Separate maps will be drawn for each species detected. Efforts will be initiated to develop a computerized mapping system on an IBM AT or DEC VAX. All data including hard copies of chromatograms will be retained indefinitely by the soil gas survey Task Manager and will be available to the Project Manager on a daily basis if needed. Summary reports include contour maps, tabular listings of data, interpretive comments, and recommendations will be written by the soil-gas survey Task Manager and provided in draft form to the Project Manager within two weeks of the completion of the survey.

REFERENCES

LaBrecque, D. J., S. L. Plerett, A. T. Baker and J. W. Hess. Hydrocarbon Plume Detection at Stove Pipe Wells, California. EPA-EMSL, 68-03-3050, Final Report, 185, 34p.

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